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(71) Applicant (*for all designated States except US*): CITY TECHNOLOGY LIMITED [GB/GB]; City Technology Centre, Walton Road, Portsmouth PO6 1SZ (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): MAKADMINI, Lothfi [TN/DE]; Alpenblick 6, D-83355 Grabenstätt (DE). HORN, Michael [DE/DE]; Rosenheimer Landstrasse 2A, D-85521 Ottobrunn (DE). TRÄNKLER, Hans-Rolf [DE/DE]; Kaiser-Ludwig-Strasse 14, D-82031 Grünwald (DE).

(74) Agent: STANLEY, David, William; Kings Court, 12 King Street, Leeds LS1 2HL (GB).

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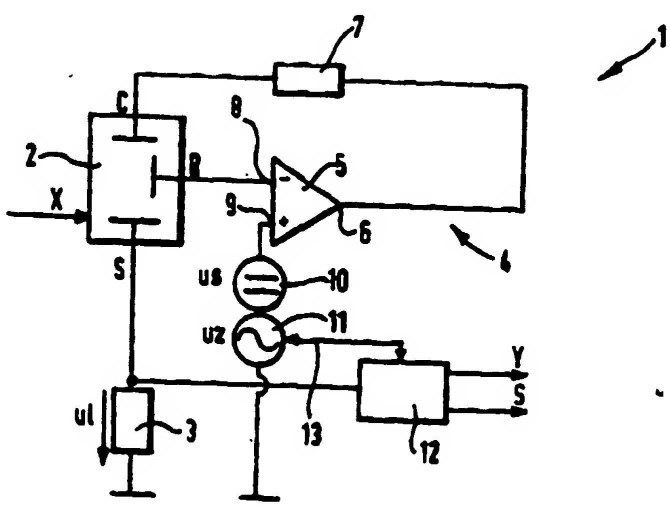

(57) Abstract

An electrochemical sensor (2), in particular, an amperometric gas sensor, is fitted with a test electrode (S), a reference electrode (R) and a counter electrode (C). The counter electrode (C) is supplied with an input alternating voltage (UZ) at a given frequency ω, and a test voltage (UL) prevailing at the test electrode (S) is evaluated. The test voltage (UL) is used to monitor a cell constant of the sensor (2), which represents the surface area of electrode that is available for electrochemical reaction. At two following time intervals, and at a given frequency ω of the input alternating voltage (UZ), the prevailing test voltages (UL) are measured and compared with one another. The frequency of the input alternating voltage (UZ) is selected in such a way that the phase displacement between the input alternating voltage (UZ) and the test voltage (UL) is small or about zero. This makes it possible to monitor the condition or functioning capability of the sensor (2).

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ELECTROCHEMICAL SENSORS

This invention relates to electrochemical sensors.

In a known method and electrical circuit for operating an electrochemical sensor, in particular an amperometric sensor, which has a test electrode, a reference electrode, an electrolyte and a counter electrode, the counter electrode is supplied by an input alternating voltage at a given frequency, and a test voltage prevailing at the test electrode is evaluated.

A method of this type as well as such an electrical circuit, are known from the publication "Elektrochemische Gassensoren - Wirkungweisen und Möglichkeiten zur Funktionsüberwachung" ("Electrochemical gas sensors-ways of working and possibilities for monitoring functions") by Dieter Kitzelmann and Carsten Gottschalk in the Journal tm - Technisches Messen 1995, No 4, pp 152-159.

Here an electrochemical sensor is described with which the concentration of a gas in air can be detected. The sensor concerned is an amperometric gas sensor, in which the gas to be detected initiates an electrochemical reaction and thereby generates an electric current. The sensor has, among other things, a counter electrode and a test electrode to which the electronic current generated flows. The electronic current is roughly proportional to the concentration of the gas under test. The electronic current is evaluated by usual means using an earthed load resistance connected to the test electrode, and appropriate signal evaluation or processing equipment.

Further, the sensor is fitted with a reference electrode which acts to stabilise the potential of the test electrode. A so-called potentiostat is used for this purpose. Its input is connected to the reference electrode, and the counter electrode to its output. A further input to the potentiostat is linked to an earthed voltage divider, over which a standard voltage can be set up. The standard voltage is dependant on the gas to be measured and can, for example, with carbon monoxide also be zero.

Impedance measurements are used for function monitoring of the sensor. Here, normally an alternating voltage is superimposed over the standard voltage, which then contributes an alternating component to the test voltage at the load resistance. This alternating component is processed further by the signal evaluation so that certain signal patterns can demonstrate a sensor failure. The problem of such a processing is that the alternating component is usually dependant on the concentration of the gas passing through the sensor.

To eliminate this effect, it is possible to carry out function monitoring with several frequencies of the alternating voltage, and to come to conclusions about sensor failure from an observation of the impedance spectrum thereby obtained. Equally, following the publication of the article quoted above, it was shown to be possible to carry out function monitoring with a single frequency to at least obtain a rough guide to the functioning capability of the sensor. At the present state of the technology, no further explanations of this latter process are available.

Preferred embodiments of the present invention aim to improve the way of operating such a sensor, and especially function monitoring procedures.

According to one aspect of the present invention, there is provided a method of operating an electrochemical gas sensor which is fitted with a test electrode, a reference electrode and a counter electrode, wherein the counter electrode is supplied with an input alternating voltage of frequency ω, and a test voltage prevailing at the test electrode is processed to provide information representative of the condition of the sensor.

Preferably, the sensor is an amperometric sensor.

Preferably, the prevailing test voltage is measured at two successive time intervals, at a given frequency of the input alternating voltage, and the values of the test voltage obtained at said successive time intervals are compared to one another.

Preferably, the frequency of the input alternating voltage is selected such that the phase displacement between the input alternating voltage and the test voltage is small or substantially zero.

Preferably, selection of said frequency of the input alternating voltage, at which the phase displacement is small or substantially zero, is effected by first applying a lower frequency and then raising this frequency.

Preferably, said lower frequency is a frequency of a few Hertz.

Preferably, the frequency of the input alternating voltage is controlled by a signal processor.

According to another aspect of the present invention, there is provided an electrochemical gas sensor and control circuit therefor, wherein

the sensor comprises a test electrode, a reference electrode and a counter electrode, and the control circuit comprises an alternating voltage source arranged to supply the counter electrode with an alternating voltage of frequency ω, and signal processing means arranged to receive a test voltage prevailing at the test electrode and to process the test voltage (UL) to provide information representative of the condition of the sensor.

Preferably, such an electrochemical gas sensor and control circuit is arranged to perform a method according to any of the preceding aspects of the invention.

An electrochemical gas sensor and control circuit as above may further comprise any one or more of the features disclosed in the accompanying specification, claims, abstract and/or drawings, in any combination.

In preferred embodiments of the present invention, the test voltage is used to monitor a cell constant of the sensor. Such a cell constant is roughly inversely proportional to the electrochemically active area of the sensor - that is, it represents the surface area of electrode that is available for electrochemical reaction. Changes in the active area of the sensor, for example, by ageing phenomena, can be recognised by the inversely proportional changes in the cell constant, and taken into consideration. Monitoring the cell constant of the sensor, it is therefore possible to control the functioning capability of the sensor, especially with reference to changes in the electrochemically active area of the sensor, and, if necessary, warn the user. This constitutes a significant improvement in function monitoring of the sensor.

In an advantageous embodiment of the invention, the input alternating voltages of the prevailing test voltages at a given frequency, are measured one after the other at two given time intervals, and compared with one another. This comparison of two test voltages makes it possible to monitor the cell constant. In particular, the first measurement of the test voltage is carried out at the start of operating the sensor, that is, when the sensor is pristine. This measured value is stored. The values measured during the sensor's operation can be compared to the stored initial value. Differences or quotients can demonstrate changes in the cell constant, and therefore a change in the electrochemically active area of the sensor.

An advantageous further development of an embodiment of the invention selects the frequency of the input alternating voltage in such a way that a phase displacement between the input alternating voltage and the test voltage is small or around zero. This limiting of the frequency of the input alternating voltage makes it possible for the test voltage to be independent of the concentration of the gas activating the sensor. In this way the test voltage generated at this frequency can be used to monitor the functioning of the sensor.

The independence of the test voltage from the concentration is achieved in that, at a smallest possible phase displacement between the input alternating voltage and the test voltage, two further factors are no longer involved. These are the concentration-dependent double layer capacity of the electrolyte, and the equally concentration-dependent double layer resistance. The test voltage is therefore essentially only still dependent on the electrolyte resistance. The specific electrolyte resistance is concentration dependant and roughly constant with time, so that electrolyte resistance is proportional to cell constant, and therefore roughly inversely proportional

to the electrochemically active area. Therefore a change in the electrolyte resistance is of equal significance to a change in cell constant, as well as a change in the electrochemically active area. This latter change can be used to interpret the functioning capability of the sensor.

An advantageous further development of an embodiment of the invention involves the initial application of a low frequency, especially a frequency of a few Hertz. This is then increased as part of the procedure to apply an input alternating voltage in which the phase displacement is small. This allows a simple, yet effective way to find and set up a frequency at which the phase displacement between the input alternating voltage and the test voltage is small, or preferably nearly zero. It is feasible that finding the frequency at which phase displacement is sufficiently small, can be undertaken by a maintenance operator.

An advantageous embodiment of the invention allows the frequency of the input alternating voltage to be set up by the signal processing or evaluation. This means that the frequency at which the phase displacement is small is determined automatically by the signal evaluation. The signal evaluation therefore affects the alternating voltage source that generates the input alternating voltage in such a way, that it just sets up a low frequency and then raises the frequency. At the same time the signal evaluation monitors the phase displacement between the input alternating voltage and the test voltage, and selects that frequency for the input alternating voltage at which the phase displacement is small or nearly zero. A fully automatic monitoring of the sensor is possible by this means, for it provides an automatic check on the functioning capability of the sensor.

An advantageous further development of an embodiment of the invention allows the frequency of the input alternating voltage at which the phase displacement is small to be set up when the sensor starts operating, and be subsequently maintained. Further, at this frequency, the impedance and the alternating component of the test voltage, respectively, are determined. This allows a later failure of the sensor to be recognised according to this embodiment of the invention.

Therefore, in the first use of the sensor, the given frequency is determined, especially automatically, and for example, stored. At the same time the test voltage and impedance, respectively are obtained and e.g. stored. Subsequently the time-and-incident-dependent behaviour of the sensor can again be monitored by using an input alternating voltage at the given frequency, and the test voltage and impedance, respectively point to a change in the sensor. In particular, the changes in test voltage and impedance, respectively can be used in conjunction with a predetermined threshold value to demonstrate a sensor failure.

This constitutes in total a special fully automatic monitoring of the sensor for its functioning capability, especially with respect to sensor failure. A defect, due e.g. to ageing phenomena or even total failure of the sensor, can be detected reliably in this way, automatically and at no great expense. A maintenance operator, for example, could be taught the procedure.

An advantageous further development of an embodiment of the invention, uses the direct component of the test voltage at the frequency of the input alternating voltage where the phase displacement is small, as output signal for the concentration of the gas activating the sensor. This

output signal is, however, still dependent on changes in the sensor, especially from ageing phenomena of the sensor.

An especially advantageous embodiment of the invention uses the direct component of the test voltage and the rectified alternating component of the test voltage multiplied together and bound into one signal. In this way it is possible to make the output signal for the concentration of gas activating the sensor independent of ageing and similar phenomena. In particular, changes in the electrochemically active area of the sensor can be monitored continuously by multiplication approaches, and their effects on sensitivity corrected. This quoted multiplicative linking is independent of the characteristic output signal that monitors the sensor's functioning capability. In particular, the output signal generated by the concentration of gas activating the sensor can still be present even when the output signal for the sensor's functioning ability is not being generated.

It is especially useful that the signal generated at the frequency of the input alternating voltage at which the phase displacement is small, is used as a corrected output signal for the concentration of gas activating the sensor. The corrected output signal gives the user information which is corrected for dependence on the size of the electrochemically active area of the sensor. This means that any changes in active area do not lead to a falsification in the corrected output signal. The quoted correction is carried out automatically and permanently, thus providing a so-called online correction. The corrected output signal gives the user information on the concentration of gas activating the sensor, which continuously and automatically equalises and corrects for possible ageing or other phenomena affecting the sensor.

Further, the previously mentioned aim of preferred embodiments of the invention is met by an electrical circuit in which the alternating voltage source and the signal evaluation or processing are linked. In this way, monitoring the cell constant of the sensor can be realised. In particular, the coupling according to this embodiment of the invention of the alternating voltage source into the signal processing or evaluation, enables the frequency of the input alternating voltage generated by the alternating voltage source to be set in such a way that the phase displacement between the input alternating voltage and the test voltage of the signal evaluation is small or nearly zero.

For a better understanding of the invention, and to show how embodiments of the same may be carried into effect, reference will now be made, by way of example, to the accompanying diagrammatic drawings, in which:

Figure 1 is a circuit diagram of a model example of an electrical circuit according to an embodiment of the invention; and

Figure 2 is a circuit diagram showing part of the model of Figure 1 in greater detail.

Figure 1 shows an electrical circuit 1 for an electrochemical sensor 2. Sensor 2 is an amperometric gas sensor which has a test electrode S (also called sensing-electrode), a reference electrode R and a counter electrode C. Sensor 2 is suitable for determining the concentration of a gas in air. Here the gas initiates an electrochemical reaction in sensor 2 that results in an electronic current flowing to the test electrode S. This electronic current is roughly proportional to the concentration of the gas to be measured. The

gas working on sensor 2 is presented in Figure 1 by an arrow, and the concentration of the gas is designated "x".

The test electrode S of sensor 2 is connected to earth via a load resistance 3. The electric current generated by the test gas flows from test electrode S over the load resistance 3 to earth, and thereby generates a test voltage UL at the load resistance 3.

Circuit 1 is fitted with a potentiostat 4, which stabilises the potential of the test electrode. The potentiostat 4 comprises an operational amplifier 5, the output 6 of which is connected to the counter electrode C of sensor 2 via a resistance 7. The inverting input 8 of the operational amplifier 5 is connected to the reference electrode R of sensor 2.

The non-inverting input 9 of the operational amplifier 5 is connected to earth via a direct voltage source 10 and an alternating voltage source 11. The direct voltage source 10 serves to set up a standard voltage US. For example, the direct voltage source 10 can be a voltage divider, connected in parallel to a direct voltage supply, with the standard voltage US being taken from roughly the middle of its range.

The operational amplifier 5 acts on the counter electrode C in such a way that the voltage difference between its inverting and non-inverting inputs 8,9, remains about zero. Thereby, the operational amplifier 5 acting via the counter electrode always sets up approximately the standard voltage US at the reference electrode R. This results in the reference electrode R, and finally also the test electrode S, remaining at a nearly constant voltage. Sensor 2 is thereby set over potentiostat 4 to a working point determined by the standard voltage US.

The alternating voltage source 11 generates an input alternating voltage UZ, with a frequency ω, which acts on sensor 2 via the non-inverting input 9 of the operational amplifier. 5. The input alternating voltage UZ is, for example, principally a sinewave, rectangular or squarewave voltage.

The test electrode S is connected to a signal processor or signal evaluation unit 12. This applies the test voltage UL to the signal processor 12. Further, the signal processor 12 is connected by a connection 13 to the alternating voltage source 11. This connection 13 allows signals to be passed in both directions. The signal processor 12 generates a signal S that provides information representative of the condition or functioning capability of sensor 2.

The monitoring of function capability of sensor 2 is carried out by an impedance measurement. The input alternating voltage UZ enables an impedance Z for sensor 2 to be measured by the signal processor 12. This impedance Z enables the signal processor 12 to provide information on the electrochemically active area of sensor 2, and thereby on its condition or functioning capability.

The following equation gives impedance Z:

$$Z(w) = RE + (RD / (1 + j \times \omega \times RD \times CD))$$

Where
- Z = impedance of sensor 2
- ω = frequency of the input alternating voltage UZ
- RE = electrolyte resistance of sensor 2
- CD = double layer capacitance of the electrolyte

RD = resistance of the double layer

j = imaginary part of the equation.

When sensor 2 begins operating, the frequency ω of the input alternating voltage UZ from the signal processor 12 is first set at a low value, via connection 13. In particular, the frequency ω comprises several Hertz. The test voltage UL is obtained from the signal processor 12. The signal processor 12 then compares the phase of the input alternating voltage UZ with the test voltage UL. If these two phases show a large phase displacement, the signal processor 12 increases the frequency ω of the input alternating voltage UZ and again compares the phases of the two above-mentioned signals. This is repeated until the phase displacement between the input alternating voltage UZ and the test voltage UL is small. In particular, this sequence is repeated until the phase displacement is nearly zero or roughly zero.

At the same time, it is possible to reduce the frequency ω of the input alternating voltage UZ even further, to find the smallest possible phase displacement. Overall, the frequency ωz that can be set by the signal processor 12 for the input alternating voltage UZ can ensure the phase displacement between the input alternating voltage UZ and the test voltage UL is small or roughly at zero.

When the phase displacement between the input alternating voltage UZ and the test voltage UL is small or approximately zero, this means that the imaginary component j of the above equation also becomes roughly zero. Therefore, the double layer capacitance CD of the electrolyte as well as the resistance RD through this double layer no longer play any part. This leads to the conclusion that the impedance Z, at the given frequency

ωz, at which the phase displacement is small or about zero, is essentially now only dependant on the electrolyte resistance RE.

The electrolyte resistance RE is independent of the concentration X of the gas activating the sensor 2. The electrolytic resistance RE is however, proportional to the so-called cell constant C, which in its turn is roughly universally proportional to the electrochemically active area of sensor 2. Therefore, the impedance Z over the electrolyte resistance RE is a measure of the magnitude of the electrochemically active area of sensor 2. If the impedance Z of sensor 2 changes, this means that the electrochemically active area of sensor 2 has changed also.

As described, the frequency ωz, at which the phase displacement between the input alternating voltage UZ and the test voltage UL is small or nearly zero, is determined by the signal processor 12 when the sensor 2 is first taken into service. This frequency ωz is stored by the signal processor 12. Further, the signal processor 12 also measures and stores the impedance ZO and the test voltage ULO at this frequency.

After this, at given intervals i, e.g. every day, the impedance Zi and the test voltage ULi at the given frequency ωz are again measured by the signal processor 12. It is likewise possible that this new measurement can be carried out by an operator over an appropriate interface, and executed by the signal processor 12. It is also possible to carry out the new measurement in some other way and in other eventualities. In every case the measured impedance Zi and test voltage ULi of the new measurement on sensor 2 will be stored by the signal processor 12.

The signal processor 12 then compares the impedance ZO and test voltage ULO of sensor 2 measurement at the start of the sensor's use, with impedance Zi and test voltage ULi, respectively, measured later. If the impedance Z and test voltage UL respectively of sensor 2 have changed, this represents a change in the cell constant C, and therefore the electrochemically active surface of sensor 2. If this change exceeds a threshold value, this means that the functioning capability of the sensor 2 can no longer be guaranteed. The signal processor 12 then registers the sensor's failure via signal S.

Alternatively or additionally, it is possible for the signal processor 12 to generate a signal Y, in which the test voltage UL is multiplied with the value of impedance Z of sensor 2. This product represents a signal free from changes in the electrochemically active area. This signal can be used to measure the gas concentration X until the signal S from the signal evaluation registers the failure of sensor 2.

Figure 2 represents that part of electrical circuit 1 which can, among other things, be used to carry out the comparison described above. In particular, the part of circuit 1 shown in Figure 2 is a part of the signal processor 12.

In a first model presentation, the test voltage UL activates an amplifier 14. Because of the direct voltage source 10 and the alternating voltage source 11, the output signal of the amplifier 14 shows both a direct component ug and an alternating component uw. Both components are fed to a high pass filter 15 which separates the alternating component uw and passes it on to a rectifier 16 and a following low pass filter 17. The output signal of the low pass filter 17 is fed to a comparator 18, which compares

this output signal ue with a signal ud. The signal ud represents the threshold value at which the signal processor 12, as described, registers the failure of sensor 2. The signal ud, for example, can be a given factor, e.g. 250% of the output signal ue, determined at the start of the sensor's working life. The output signal of the comparator 18 is then the signal S, with which the signal processor 12 (if necessary) registers a failure.

Therefore, the alternating component uw is decoupled from the test voltage UL, and rectified. The threshold value ud is derived from the output signal ue of sensor 2 when it first begins operating. Subsequent measurements of the output signal are determined and compared with ud. When the output signal ue reaches the threshold value ud, the signal S changes, and informs an operator of the failure of sensor 2.

In a further model presentation, the direct component ug and the alternating component uw of the output signal of the amplifier 14 are fed to a low pass filter. Further, the multiplier 20 is activated by the output signal ue of the low pass filter 17. The multiplier 20 produces a signal Y from both the direct component ug and the output signal ue, that corresponds to the corrected concentration value x of the gas activated in sensor 2. An operator can read off the concentration of the measured gas from signal Y.

The determination of signal Y is thereby independent of the determination of signal S; it can therefore also be carried out when signal S is not generated by circuit 1. Signal Y represents an output signal which is corrected with respect to the electrochemically active area of sensor 2. This means that a change of the active area is taken into account by signal Y, and therefore cannot lead to a falsification of signal Y. The quoted correction

takes place automatically and permanently by means of the signal ue, so that a so-called online correction is present.

Signal Y not only gives a user information on the concentration of the gas activated in sensor 2, but also monitors continuously possible ageing phenomena or the like of sensor 2, and automatically corrects them.

The term "ground potential" (or like terms such as "ground voltage" or "earth" potential or voltage) is used conveniently in this specification to denote a reference potential. As will be understood by those skilled in the art, although such reference potential may typically be zero potential, it is not essential that it is so, and may be a reference potential other than zero.

In this specification, the verb "comprise" has its normal dictionary meaning, to denote non-exclusive inclusion. That is, use of the word "comprise" (or any of its derivatives) to include one feature or more, does not exclude the possibility of also including further features.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of operating an electrochemical gas sensor (2) which is fitted with a test electrode (S), a reference electrode (R) and a counter electrode (C), wherein the counter electrode (C) is supplied with an input alternating voltage (UZ) of frequency (ω), and a test voltage (UL) prevailing at the test electrode is processed to provide information representative of the condition of the sensor.

2. A method according to claim 1, wherein the sensor is an amperometric sensor.

3. A method according to claim 1 or 2, wherein the prevailing test voltage (UL) is measured at two successive time intervals, at a given frequency (ω) of the input alternating voltage (UZ), and the values of the test voltage (UL) obtained at said successive time intervals are compared to one another.

4. A method according to any of the preceding claims, wherein the frequency (ω) of the input alternating voltage (UZ) is selected such that the phase displacement between the input alternating voltage (UZ) and the test voltage (UL) is small or substantially zero.

5. A method according to claim 4, wherein selection of said frequency (ω_Z) of the input alternating voltage (UZ), at which the phase displacement is small or substantially zero, is effected by first applying a lower frequency (ω) and then raising this frequency (ω).

6. A method according to claim 5, wherein said lower frequency is a frequency (ω) of a few Hertz.

7. A method according to any of the preceding claims, wherein the frequency (ω) of the input alternating voltage (UZ) is controlled by a signal processor (12).

8. A method of operating an electrochemical gas sensor, the method being substantially as hereinbefore described with reference to Figure 1 or Figures 1 and 2 of the accompanying drawings.

9. An electrochemical gas sensor and control circuit therefor, wherein the sensor comprises a test electrode (S), a reference electrode (R) and a counter electrode (C), and the control circuit comprises an alternating voltage source (11) arranged to supply the counter electrode (C) with an alternating voltage (UZ) of frequency (ω), and signal processing means (12) arranged to receive a test voltage (UL) prevailing at the test electrode and to process the test voltage (UL) to provide information representative of the condition of the sensor.

10. An electrochemical gas sensor and control circuit according to claim 9, arranged to perform a method according to any of claims 1 to 8.

11. An electrochemical gas sensor and control circuit according to claim 9 or 10, further comprising any one or more of the features disclosed in the accompanying specification, claims, abstract and/or drawings, in any combination.

12. An electrochemical gas sensor and control circuit, substantially as hereinbefore described with reference to Figure 1 or Figures 1 and 2 of the accompanying drawings.

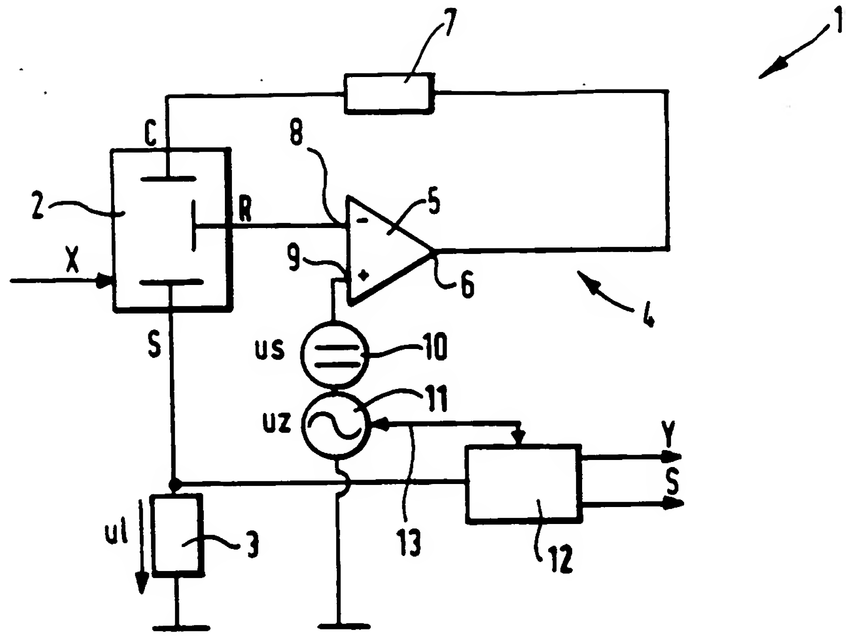
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Fig.1.

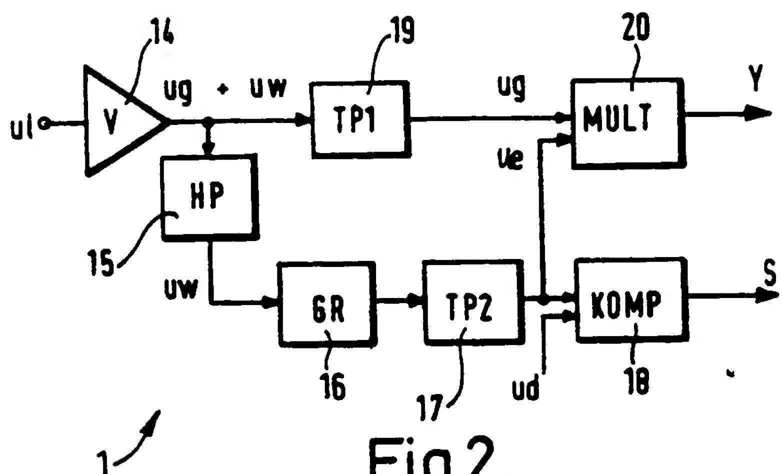
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Fig.2.

INTERNATIONAL SEARCH REPORT

Int[illegible]ional Application No
PCT/GB 98/02967

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/416

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 43 18 891 A (MANNESMANN AG) 8 December 1994 see column 3, line 10 - line 33 ---	1,8,9,12
Y	WO 90 12315 A (NEOTRONICS LTD) 18 October 1990 see page 6, line 1 - page 7, line 4 ---	1,8,9,12
A	US 3 661 748 A (BLACKMER DAVID E) 9 May 1972 see abstract ---	1
A	CH 636 447 A (CIBA GEIGY AG) 31 May 1983 see abstract ---	1
A	EP 0 497 994 A (KNICK ELEKTRONISCHE MESSGERAET) 12 August 1992 see figure A ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 January 1999	16/02/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Duchatellier, M

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02967

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 32 39 572 A (HORIBA LTD) 26 May 1983 see figure A	1
A	WO 93 08477 A (ROSEMOUNT ANALYTICAL INC) 29 April 1993 see figure A	1
A	L. MAKADMINI: "SELF-CALIBRATING ELECTROCHEMICAL SENSOR" 1997 INTERNATIONAL CONFERENCE ON SOLID-STATE SENSORS AND ACTUATORS, vol. 1, April 1997, pages 299-302, XP002091408 CHICAGO, US see the whole document	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/02967

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4318891 A	08-12-1994	EP 0628810 A	14-12-1994
WO 9012315 A	18-10-1990	AU 5335390 A	05-11-1990
		CA 2051099 A	05-10-1990
		DE 69023129 D	23-11-1995
		DE 69023129 T	18-04-1996
		EP 0467902 A	29-01-1992
		JP 4504307 T	30-07-1992
		US 5202637 A	13-04-1993
US 3661748 A	09-05-1972	NONE	
CH 636447 A	31-05-1983	NONE	
EP 0497994 A	12-08-1992	DE 59105178 D	18-05-1995
DE 3239572 A	26-05-1983	JP 58092854 A	02-06-1983
		JP 63016706 B	11-04-1988
WO 9308477 A	29-04-1993	US 5268852 A	07-12-1993
		CA 2119435 A	29-04-1993
		DE 69223640 D	29-01-1998
		DE 69223640 T	02-07-1998
		EP 0609334 A	10-08-1994
		JP 7500419 T	12-01-1995